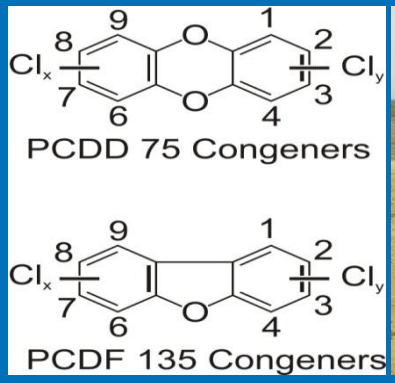
EPA
United States
Environmental Protection
Agency

Bioremediation Potential for Dioxin

RTP, NC
November 2013



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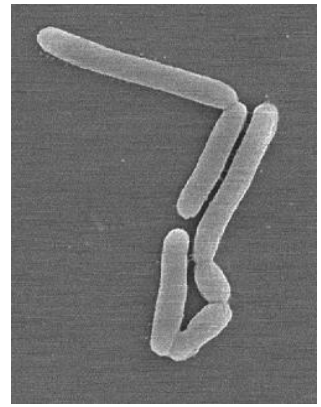
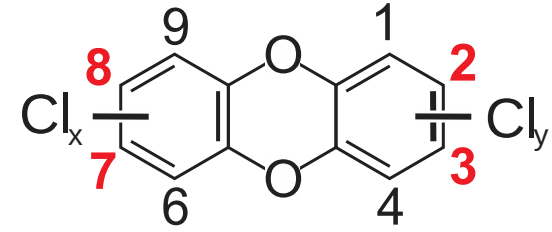
Presentation Overview

- Overview of dioxins
- Dioxin bioremediation fundamentals
- Current understanding of dioxin bioremediation
  - performance of differing pathways
  - selecting appropriate bioremediation methods
- EPA findings and recommendations
- Conclusions
- Future research needs

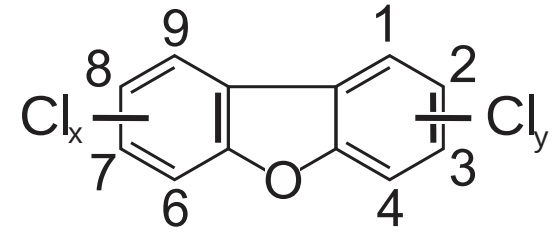


Overview of Dioxins

- **Dioxins - chlorinated benzene rings linked by ether bridge, congeners share characteristics:**
  - **environmental persistence (soil and sediment)**
  - **bioaccumulation potential (lipophilic)**
  - **toxicity mechanisms**
- **Over 200 congeners known**
  - **most studied conger is 2,3,7,8-TCDD (tetrachlorodibenzo-*p*-dioxin)**



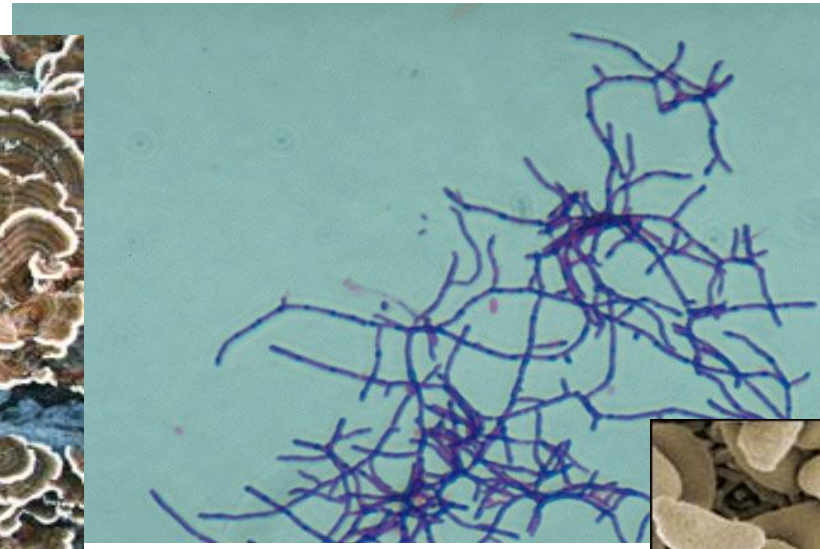
PCDD 75 Congeners



PCDF 135 Congeners

Dioxin Bioremediation Fundamentals

Bioremediation: the exploitation of living microorganisms (bacteria and fungi) to convert hazardous compounds or chemicals into carbon dioxide, water, less or non-hazardous chemicals, and biomass



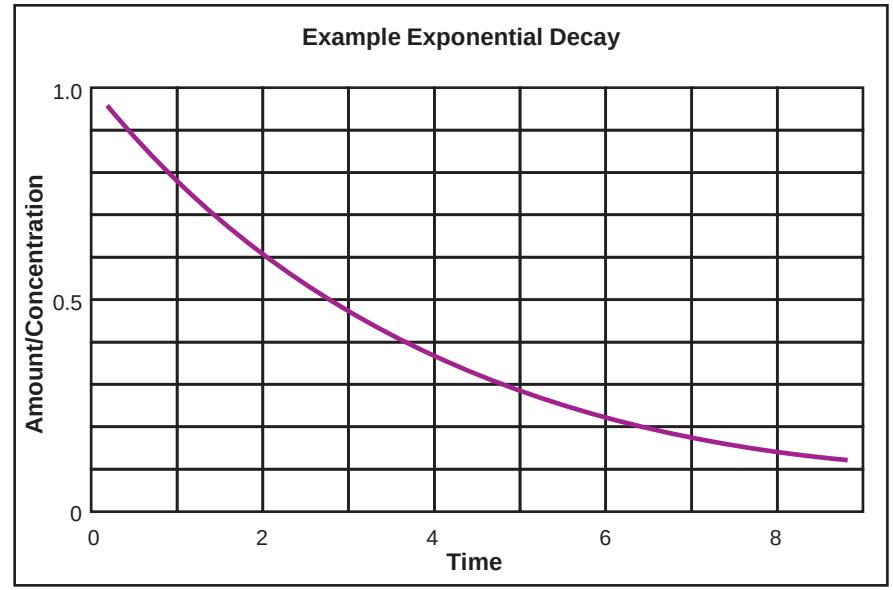
L to R: White rot fungi, *Actinomycetes* (bacteria), C*ladosporium* (fungi), *Dehalococcoides* (bacteria)

Current Understanding of Dioxin Bioremediation

- Variety of bacteria and fungi studied from the available English language literature
- Focus has been individual dioxin congener biodegradation
- Laboratory studies indicate aerobic breakdown can biotransform ‘lightly’ chlorinated dioxins via oxidation (less than 4 chlorine atoms)
- Predominant biotic transformation pathway for ‘highly’ chlorinated dioxins (4 or more chlorine atoms) is anaerobic reductive dechlorination

Current Understanding of Dioxin Bioremediation

- **Estimated dioxin half-lives with biological treatment:**
  - **field; years**
  - **laboratory; months**
- **Dioxin degradation rates in the field are:**
  - **highly variable**
  - **usually less than in laboratory**
- **No available English language studies using only bioremediation for field-scale dioxin decontamination**

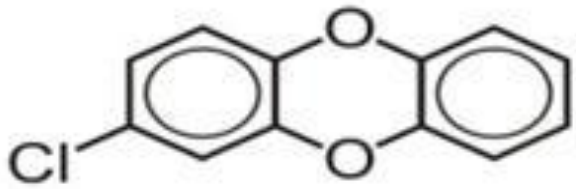


Performance of Differing Biodegradation Pathways

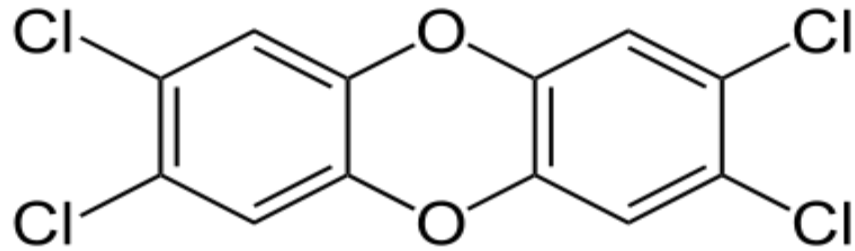
- **Understanding specific biological reductive dechlorination and subsequent biooxidation pathways for specific congeners or mixtures is important before conducting field-scale remediation**

Performance of Differing Pathways (Aerobic)

- **Oxidative process where aromatic rings are cleaved with the resulting by-products either biotransformed or completely mineralized**
- **Only lightly chlorinated dioxins (< 4 chlorines) amenable for aerobic biotransformations**



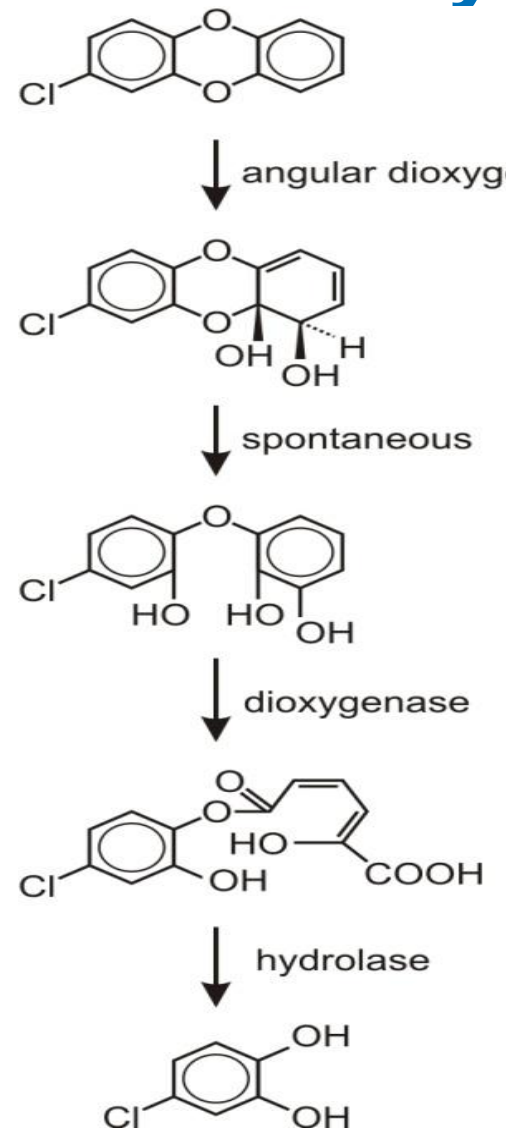
Likely candidate for aerobic biotransformation

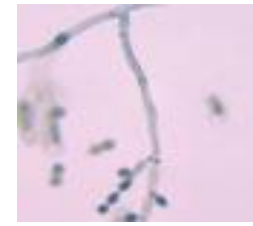


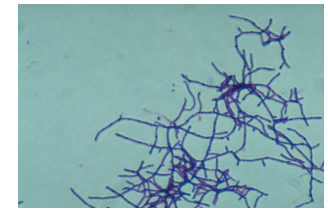
Less likely candidate for aerobic biotransformation

Performance of Differing Pathways (Aerobic)

Proposed aerobic biotransformation pathway – an enzymatic reaction inserts oxygen into the dioxin molecule, changing the structure of the aromatic ring and breaking the ether bridge (note 'light' chlorination)





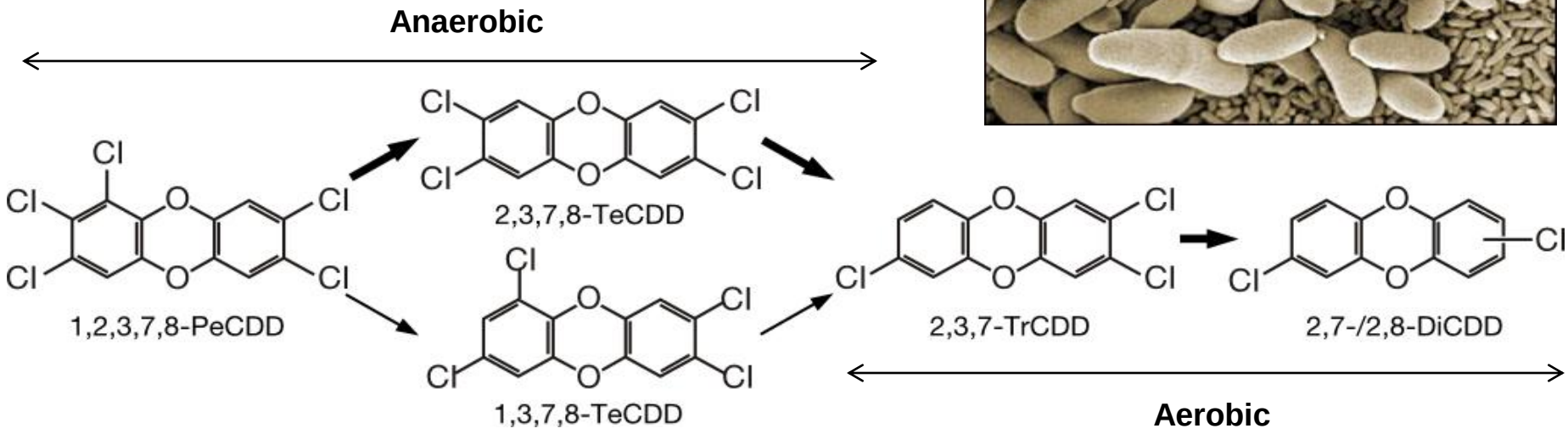


Performance of Differing Pathways (Anaerobic)

- **Reductive dechlorination process that sequentially removes chlorines from dioxin aromatic rings**
- **Highly chlorinated dioxin preferentially degraded**
- **Understanding dechlorination pathway of highly chlorinated dioxin is important for knowing and controlling by-products**

Performance of Differing Pathways (Anaerobic)

- **Proposed pathway for dechlorination (ex. 1,2,3,7,8-PeCDD)**



- **Lightly chlorinated dioxin by-products are then ready for aerobic biodegradation**

Selecting Appropriate Bioremediation Methods

Concentration important for biotransformation

- Enzymatic degradation based on concentration
- Low concentration = little or no enzymes, so slow or no remediation
- Studies are in 10-100's of ppb to support degradation
- Target goals for cleanup (< 5 ppb) are at low end of concentrations where bioremediation has been investigated

Selecting Appropriate Bioremediation Methods

Congener of dioxin impact biotransformation

- Dioxin can closely associate/bond with organic matter in soil and sediment
  - decreases bioaccessibility and biodegradation rates

Findings from Past EPA Studies

Bioremediation regarded as having potential for dioxin, but applicability and effectiveness is not known

- EPA has had mixed success with bioremediation for polychlorinated biphenyls (PCB) remediation, and less success with dioxin
- Fungi and anaerobic bacteria appear somewhat promising
  - concentrations in experiments were high (ppm to ppb range), and results have been highly variable
- Solubility of dioxin is another limiting factor

Findings from Past EPA Studies

Technical obstacles limiting application of bioremediation:

- **Only specialized biological systems appear effective for dioxin**
- **Very stringent (low) cleanup concentration must be met (1 ppb for residential use), studies have all been with much higher concentrations**
- **May be difficult to find microorganism(s) in the environment that remediate dioxins under different conditions present at sites**

Recommendations Based on Past EPA Studies

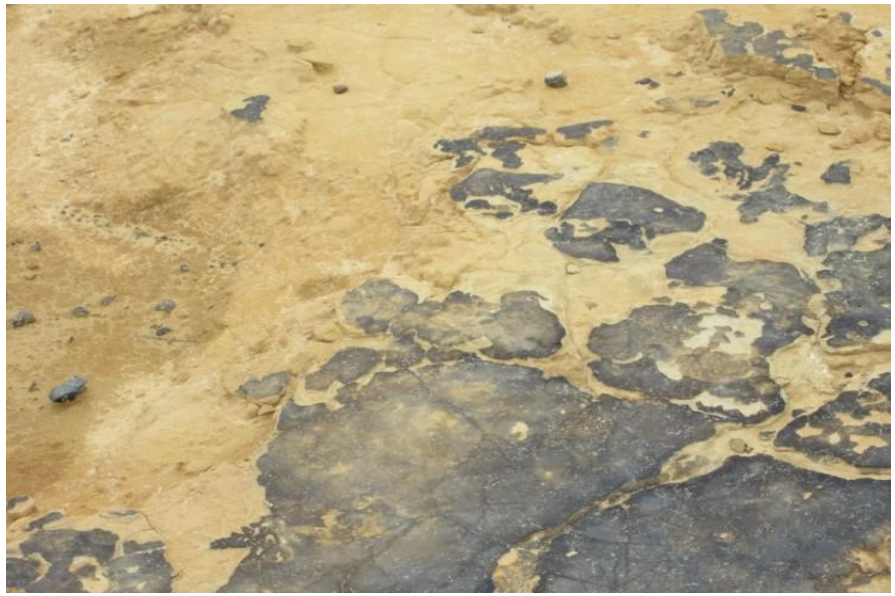
Findings from past studies indicate that we need additional bench-, pilot-, and field-scale treatability studies to better understand:

- **Enzyme processes**
- **Chemical mechanisms**
- **Facultative biological relationships**
- **Site characteristic effects (location, soil type, pH, temperature…)**
- **Effect of co-contaminants (metals, other chemicals)**

Dioxin Research and Applications at EPA

NCEA completed comprehensive human health and exposure assessment for dioxin

- **Reviewed dioxin soil clean-up levels currently in use across the U.S. (non-cancer endpoint)**



Dioxin Research and Applications at EPA

- For > 200 Superfund NPL sites that have dioxin contamination in surface and subsurface soils, most used the following remedies:
  - landfill disposal
  - thermal treatment
- Dioxin remedy selection based on:
  - ability to meet cleanup levels
  - cost/performance analysis

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Conclusions

- State of bioremediation knowledge is not advanced to the point where it can be an accepted remedy in the U.S.
- No known single biological pathway to mineralize highly-chlorinated dioxins
- State-of-science dioxin bioremediation is at bench-scale (infancy)

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Future Research Needs

To support full-scale bioremediation of dioxins, advances and demonstrations are needed:

- **Demonstration of remediation at relevant (low) environmental concentrations and within relevant media (i.e., soil and sediments)**
- **Demonstration of two (or more) stage remediation technologies that include bioremediation**
- **Advanced methods to document remediation in biotransformation pathway(s)**

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Future Research Needs

- **Better understanding of biological pathways**
- **Demonstrated sequential anaerobic/aerobic remediation of highly chlorinated dioxin**
- **New, affordable methods for:**
  - **Laboratory - specific dioxin isotope analysis**
  - **Field - development/use of bioassays**


Thank you!
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